

Research Article

Phase Composition of Ni/Mg_{1-x}Ni_xO as a Catalyst Prepared for Selective Methanation of CO in H₂-Rich Gas

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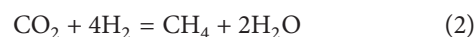
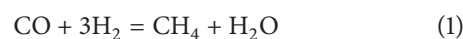
Supported Ni catalysts Ni/Mg_{1-x}Ni_xO were prepared by reducing samples NiO-MgO in H₂/N₂ mixture gas at 500°C~800°C for selective methanation of CO in H₂-rich gas (CO-SMET). The samples NiO-MgO were obtained by heating water slurry of MgO and Ni(NO₃)₂ in a rotary evaporator at 80°C and a final calcination in air at 400°C~800°C. X-ray diffraction (XRD) and temperature programmed reduction (TPR) measurements demonstrate that the samples NiO-MgO were composed of solid solution Mg_{1-y}Ni_yO as the main phase and a minor amount of NiO at calcination temperature of 400°C, and amount of the NiO was decreased as calcination temperature increased. Phase composition of the catalysts Ni/Mg_{1-x}Ni_xO was estimated by the Rietveld method. Effects of reduction temperature, feed Ni/Mg ratio, and calcination temperature on phase composition and catalytic activity of the catalysts were investigated. It is clear that CO conversion was generally enhanced by an increased amount of metallic Ni of the catalysts.

1. Introduction

NiO and MgO have similar crystal structure, so an ideal solid solution Mg_{1-y}Ni_yO (1 ≥ y ≥ 0) can be formed [1]. Calcination at 650°C or higher is beneficial for formation of the solid solution [2, 3]. It is also reported that at calcination temperature of 500°C the solid solution was formed without or with formation of a minor amount of NiO [4, 5]. It appears that a uniform dispersion of the two kinds of metallic ions in precursor allows the solid solution formed at a lower calcination temperature [6]. Ni²⁺ ions in the solid solution are hard to be reduced in comparison to Ni²⁺ ions in NiO [2, 3, 6, 7]. In a usual reduction process, only a part of Ni²⁺ ions can be reduced from the solid solution, and the Ni crystallites formed in such a way have smaller sizes and are isolatedly distributed on the surface of the remaining solid solution [3, 8]. Owing to this unique feature, the solid solution is studied extensively as catalyst precursor for CO₂ reforming reaction of methane these years [8, 9]. The CO₂ reforming reaction suffers from serious carbon deposition on the conventional Ni catalyst commercially used for the steam reforming reaction and has no industrial process so far [8]. Coke deposit was less on the Ni catalyst prepared from reduction of the

solid solution due to the small size and uniformly distributed Ni crystallites [8].

Supported Ni catalyst is also effective for selective methanation of CO in H₂-rich gas (CO-SMET) to produce fuel gas with CO content below 100 ppm for proton exchange membrane fuel cell (PEMFC) [10]. The H₂-rich mixture gas produced by the industrial processes, that is, steam reforming of hydrocarbons and the following water-gas shift reaction, is largely composed of 0.5%~2% CO, 15%~20% CO₂, more than 65% H₂, and a quantity of steam (volume percent). Presence of CO at the level will cause poisoning of the anode of the PEMFC. So it is desirable to remove CO by selective methanation of CO in the H₂-rich gas as (1). Hydrogenation of CO₂ into CO and/or CH₄ must be avoided or suppressed to a permissible level, because it consumes more H₂ and thus lowers H₂ concentration in the fuel gas seriously (2):



Both kinds of support and preparation method affect catalytic activity [10, 11]. Takenaka et al. prepared a series of Ni supported catalysts by impregnation method and found that catalytic activity for CO-SMET was in the order of support ZrO₂,

TiO₂ > SiO₂ > Al₂O₃ > MgO [11]. The catalyst Ni/MgO had the lowest activity among the catalysts, with a CO conversion less than 5% at reaction temperature of 250°C. In the present work, we are intended to take advantage of the property of the solid solution to prepare Ni/Mg_{1-x}Ni_xO catalysts for CO-SMET. For this purpose, water slurry of MgO and Ni(NO₃)₂ was used to prepare the initial precursor, and then the dried precursor was calcined in air at different temperatures to obtain NiO-MgO sample. The extent to which solid solution was formed in the sample NiO-MgO was analyzed. With a following reduction treatment in H₂/N₂ mixture gas, a part of Ni²⁺ ions in the sample NiO-MgO was reduced into metallic Ni, forming Ni supported catalyst Ni/Mg_{1-x}Ni_xO. Metallic Ni content in the catalyst was estimated by the Rietveld method. Effects of reduction temperature, feed Ni/Mg ratio, and calcination temperature on phase composition and catalytic activity of the catalysts were investigated.

2. Experimental

2.1. Preparation of Samples NiO-MgO. 5 g MgO powder (Analytical grade, Shanghai Guoyao Chemicals, China) was added into 30 mL deionized water under rigorous stirring. Meanwhile a required amount of nickel nitrate (Analytical grade, Beijing Tongguang Fine Chemicals, China) was dissolved in 20 mL deionized water. The solution of nickel nitrate was added dropwise into the water slurry of MgO, and stirring was kept for 15 min after the addition. The resulting slurry of MgO with Ni(NO₃)₂ was subsequently heated in a rotary evaporator at 80°C and vacuum degree of 0.08 MPa for 35 min to vaporize the excessive water. The wet solid obtained was dried in an oven at 110°C for 4 h. At last, the dried sample was calcined at a set temperature (400°C~800°C) for 2 h in a muffle furnace in static air. The calcined sample is denoted as *m*NiO-MgO-*T_c*, where *T_c* is calcination temperature (400°C~800°C) and the variable *m* is weight percent of the two fed chemicals expressed by the mass ratio of Ni/MgO (*m* = 10%~40%).

2.2. Characterizations. Thermogravimetric (TG) curve was recorded on a thermogravimetric analyzer (Shimadzu, DTG-60) for the dried samples obtained above to determine a proper calcination temperature (*T_c*). About 3 mg sample was loaded and heated from room temperature to 800°C at 10°C/min in air flow of 30 mL/min.

Specific surface area (SSA) of the calcined samples was measured on an adsorption-desorption analyzer (JW-DA, Beijing JWGB Sci. & Tech., China). At first the sample was degassed at 150°C for 1 h in high vacuum and then allowed to adsorb N₂ at liquid nitrogen temperature (-196°C) under a relative pressure of *p/p*₀ = 0.06~0.30. The BET equation was used to calculate SSA value.

Temperature programmed reduction (TPR) measurement was conducted for the calcined samples on a TPR instrument (PX200, Tianjin Pengxiang Sci. & Tech. Co., China) equipped with a thermal conductivity detector (TCD). 20.0 mg of the calcined sample was loaded in a quartz tube and heated in 10% H₂/Ar mixture gas (40 mL/min)

to 700°C at 10°C/min. The measurement was repeated for every sample. Deviation of TPR peak area of a measurement to the average of the duplicate measurements is within 5%. Response factor of the TPR instrument under the measurement condition was determined by use of NiO powder as standard material according to reaction NiO + H₂ = Ni + H₂O.

Phase identification was done on an X-ray diffractometer (D8 Advance, Bruker) with Cu Kα irradiation at 40 kV and 40 mA. X-ray diffraction (XRD) pattern was recorded from 30° to 85° (2θ) at a scan rate of 1°/min. The Rietveld refinement method implemented in the TOPAS software package was used to estimate phase composition of the catalyst Ni/Mg_{1-x}Ni_xO and crystal domain size of the support (i.e., the remaining solid solution Mg_{1-x}Ni_xO). The Scherrer equation was used to estimate thickness of Ni crystallites on the plane (200) (2θ = 52.1°) by use of the full width at the half maximum of the XRD peak.

Atomic ratios of Ni/Mg of the calcined samples were measured on an ICP spectrometer (Thermo Scientific, iCAP 6000 Series). The measured values of the atomic ratio of Ni/Mg are 0.070, 0.137, 0.203, and 0.262 for the samples with *m* = 10%, 20%, 30%, and 40%, respectively. These values are close to the values of 0.068, 0.136, 0.203, and 0.271 calculated from the amounts of the fed chemicals.

2.3. Catalytic Activity Evaluation. 200 mg of the calcined sample *m*NiO-MgO-*T_c* (40–60 mesh) was loaded into a quartz tube (8 mm i.d.) and fixed between two quartz wool plugs. Reduction treatment was conducted in H₂/N₂ mixture gas (fixed at 100 mL/min) with temperature increasing from room temperature to a set temperature (500°C~800°C) and holding at the set temperature for 2 h. The reduced sample is denoted as *m*Ni/Mg_{1-x}Ni_xO-*T_c*-*T_r*, in which *T_r* is reduction temperature (500°C~800°C), and the variables *m* and *T_c* are the same as above.

Catalytic activity of the reduced sample Ni/Mg_{1-x}Ni_xO as catalyst for CO-SMET was evaluated at atmospheric pressure by switching to a simulated H₂-rich gas, of which volume composition is 1.0% CO, 18.0% CO₂, 70.0% H₂, and 11.0% N₂, flowing at 50 mL/min. Reaction products were analyzed after 1 h of reaction at a set reaction temperature with a thermal conductivity detector (TCD) on a gas chromatograph (GC9800, Shanghai Kechuang, China), in which a packed column (Shincarbon ST, Shimadzu Column Packing, Japan) was connected to separate N₂, CO, CH₄, and CO₂. No hydrocarbon except CH₄ was formed in the CO-SMET reactions. The measurement was repeated for every sample. Deviation of catalytic activity data of a measurement to the average of the duplicate measurements is within 5%. CO conversion (*X_{CO}*), CO₂ conversion (*X_{CO₂}*), and selectivity of CO methanation (*S_{CH₄}*) in the CO-SMET reaction are calculated according to (3)–(5), where the subscripts 0 and 1 denote the concentrations of a component at the inlet and the outlet of the reactor, respectively:

$$X_{\text{CO}} = \frac{([\text{CO}]_0 / [\text{N}_2]_0 - [\text{CO}]_1 / [\text{N}_2]_1)}{([\text{CO}]_0 / [\text{N}_2]_0)} \times 100\%, \quad (3)$$

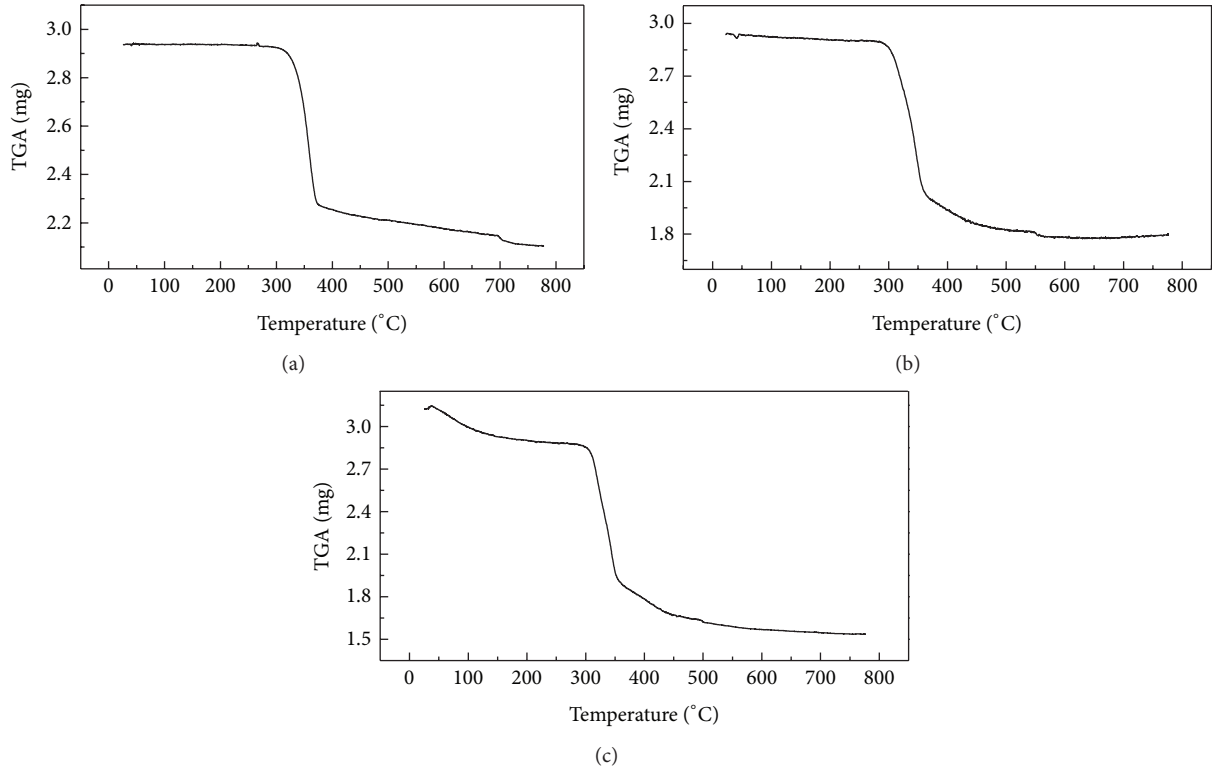


FIGURE 1: TG curves of the dried samples with $m = 0\%$ (a), 20% (b), and 40% (c), respectively.

$$X_{\text{CO}_2} = \frac{([\text{CO}_2]_0 / [\text{N}_2]_0 - [\text{CO}_2]_1 / [\text{N}_2]_1)}{([\text{CO}_2]_0 / [\text{N}_2]_0)} \times 100\%, \quad (4)$$

$$S_{\text{CH}_4} = \frac{X_{\text{CO}}}{(X_{\text{CO}} + 18X_{\text{CO}_2})} \times 100\%. \quad (5)$$

3. Results and Discussion

3.1. Phase Composition of the Calcined Samples NiO-MgO. Figure 1 shows thermogravimetric (TG) curves of the dried samples before calcination. Curve (a) was recorded for the sample dried from the water slurry of MgO powder without adding nickel nitrate (i.e., $m = 0\%$) for comparison, its weight loss being about 29 wt%, close to the theoretic value of 31 wt% of decomposition of $\text{Mg}(\text{OH})_2$ into MgO. This indicates that MgO hydrolyzed into $\text{Mg}(\text{OH})_2$ during the heating process in the rotary evaporator at 80°C for 35 min. Yoshida et al. also confirmed by XRD measurement that MgO changed completely to $\text{Mg}(\text{OH})_2$ by adding water [4]. Weight losses of curves (b) and (c) in Figure 1 correspond to decomposition of hydroxides and nitrates into oxides of the two kinds of metallic ions. Since weight loss of the dried samples occurred in $300^\circ\text{C} \sim 400^\circ\text{C}$, the lowest calcination temperature (T_c) was chosen at 400°C . Figure 2 shows XRD patterns of the calcined samples $m\text{NiO-MgO-400}$ ($m = 10\% \sim 40\%$). Because NiO and MgO have similar crystal structure, their XRD peaks are overlapped and solid solution $\text{Mg}_{1-y}\text{Ni}_y\text{O}$ ($1 \geq y \geq 0$) can be formed [1]. Yoshida et al. claimed that their NiO-MgO

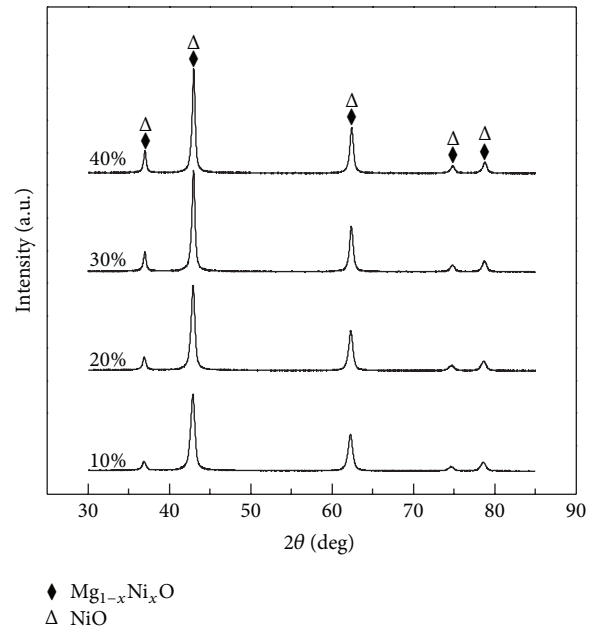
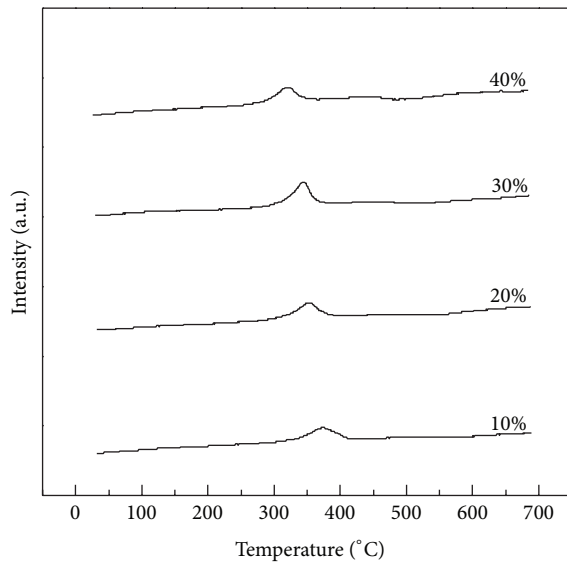


FIGURE 2: XRD patterns of the samples $m\text{NiO-MgO-400}$ ($m = 10\% \sim 40\%$).

system prepared by impregnation method is a complete solid solution after calcination at 500°C for 4 h [4]. Meshkani et al. argued that an amount of NiO may be present besides the main phase of the solid solution in their samples calcined at

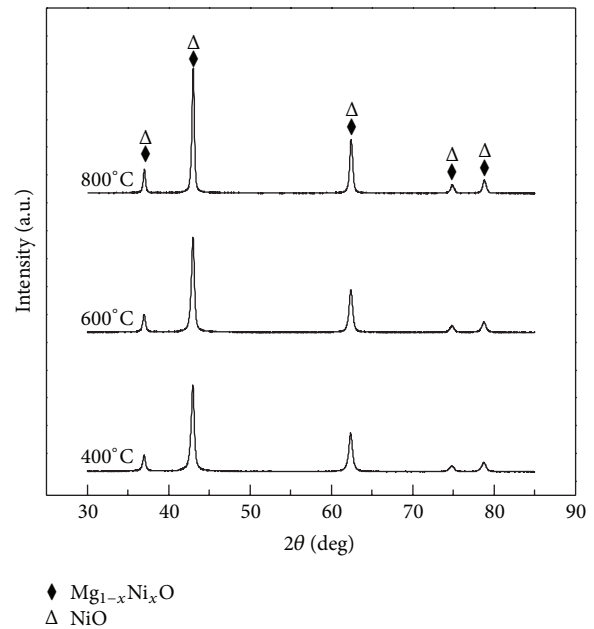
TABLE 1: Phase composition and specific surface area (SSA) of the samples $m\text{NiO-MgO-}T_c$.

Sample	SSA (m^2/g)	Phase composition (wt%)		Feed composition (wt%)	
		$\text{Mg}_{1-y}\text{Ni}_y\text{O}$	NiO	MgO	NiO
10%NiO-MgO-400	73	98.13	1.87	88.52	11.48
20%NiO-MgO-400	55	98.08	1.92	79.77	20.23
30%NiO-MgO-400	40	97.63	2.37	72.67	27.33
40%NiO-MgO-400	38	97.81	2.19	67.31	32.69
30%NiO-MgO-600	40	>99.5	<0.5	72.67	27.33
30%NiO-MgO-800	26	~100	—	72.67	27.33

FIGURE 3: TPR profiles of the samples $m\text{NiO-MgO-}400$ ($m = 10\% \sim 40\%$).

500°C for 4 h [5]. In the present work, the samples $m\text{NiO-MgO-}400$ ($m = 10\% \sim 40\%$) were prepared from calcination of the uniform precursors formed in a rotary evaporator at 80°C for 35 min. So it is reasonable to believe that the samples $m\text{NiO-MgO-}400$ ($m = 10\% \sim 40\%$) are composed of two phases of solid solution and NiO. Their phase compositions were thus tried to be fitted by the Rietveld method. However, a large uncertainty in phase composition was observed due to the XRD peak overlapping of NiO with the solid solution phase.

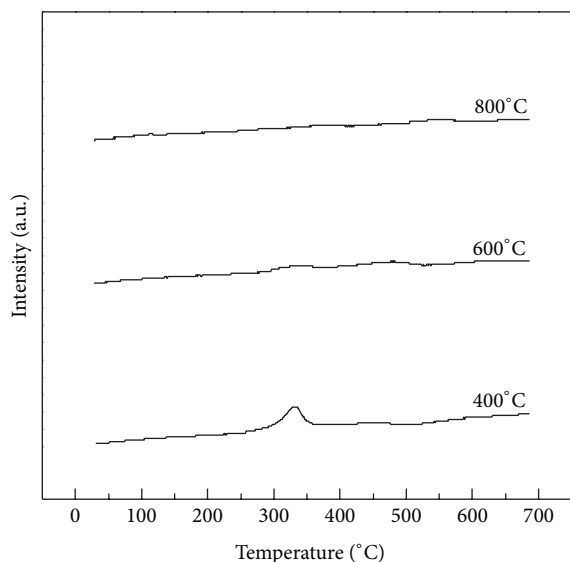
Figure 3 shows TPR curves of the calcined samples $m\text{NiO-MgO-}400$ ($m = 10\% \sim 40\%$). A small TPR peak appeared in 300°C~400°C for all the four samples, corresponding to reduction of NiO. It is reported that reduction of solid solution $\text{Mg}_{1-y}\text{Ni}_y\text{O}$ needs a high temperature, largely in 400°C~700°C for reduction of Ni^{2+} ions in subsurface layer of the solid solution, at 800°C and higher for reduction of Ni^{2+} ions in the bulk, and also a period of time at the high temperatures is needed for the reduction to be completed due to its low reduction rate [3, 7, 12]. In order to study influence of calcination temperature on formation of solid solution, higher calcination temperatures of 600°C and 800°C

FIGURE 4: XRD patterns of the samples $30\%\text{NiO-MgO-}T_c$ ($T_c = 400^\circ\text{C} \sim 800^\circ\text{C}$).

were adopted. Figure 4 shows XRD patterns of the samples $30\%\text{NiO-MgO-}T_c$ ($T_c = 400^\circ\text{C} \sim 800^\circ\text{C}$). TPR curves of this series samples are presented in Figure 5. No obvious reduction peak can be seen for the samples calcined at 600°C and higher, indicating a greater extent of formation of solid solution had been achieved. This is consistent with the publications [2, 3]. On an assumption that solid solution $\text{Mg}_{1-y}\text{Ni}_y\text{O}$ was not reduced notably in the dynamic process of TPR measurement, phase composition of the calcined samples was estimated by use of the TPR peak areas. The results are listed in Table 1. Similar TPR analyses to calculate degree of reduction of a sample were reported in literatures [3, 7]. Feed compositions expressed on formulas of MgO and NiO of the calcined samples are also given in Table 1 according to the Ni/Mg atomic ratios measured by ICP for comparison. It is clear that a major portion of the fed Ni^{2+} ions had incorporated into MgO crystal lattice forming solid solution $\text{Mg}_{1-y}\text{Ni}_y\text{O}$ even at the calcination temperature of 400°C. This is supported by the single XRD peak at $2\theta = 62.4^\circ, 74.7^\circ, \text{ and } 78.7^\circ$ in Figure 2. If there was an appreciable amount of NiO in the samples,

TABLE 2: Effect of reduction temperature ($T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$) on phase composition of the catalysts $20\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-T_r$.

T_r ($^\circ\text{C}$)	$\text{Mg}_{1-x}\text{Ni}_x\text{O}$			Phase composition (wt%)			DR (%)	Ni $D(200)$ (nm)	Ni/Mg atomic ratio	
	x	a (\AA)	R (nm)	$\text{Mg}_{1-x}\text{Ni}_x\text{O}$	Ni	Error			Fitted	Feed
500	0.0926	4.2136	23.5	99.33	0.67	0.32	5.1	—	0.108	0.137
600	0.0911	4.2131	26.0	97.68	2.32	0.23	16.2	—	0.120	0.137
700	0.0823	4.2112	32.1	96.15	3.85	0.29	26.3	13.5	0.122	0.137
800	0.0591	4.2105	42.6	93.96	6.05	0.20	44.0	13.1	0.112	0.137

FIGURE 5: TPR profiles of the samples $30\%\text{NiO}-\text{MgO}-T_c$ ($T_c = 400^\circ\text{C}\sim 800^\circ\text{C}$).

the XRD peaks at the angles would be double peaks, one belonging to NiO phase [13]. Table 1 indicates that a higher calcination temperature is more favorable for solid solution formation. But, calcination at 800°C led to a noticeable decrease in specific surface area (SSA). And also SSA value decreased with increasing content of Ni^{2+} ions. This is in agreement with the results in literatures [13, 14].

3.2. Effect of Reduction Temperature. A series of catalysts $20\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-T_r$ ($T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$) were prepared by reducing the calcined sample $20\%\text{NiO}-\text{MgO}-400$ with $70\% \text{H}_2/\text{N}_2$ mixture gas at the reduction temperature $T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$, respectively. Conversions of CO and CO_2 over the catalysts are shown in Figure 6. It is seen that higher reduction temperature is advantageous to methanation of CO and CO_2 . At reaction temperature below 240°C , CO_2 was not converted. This is in agreement with literatures [15–17] and attributed to preferential adsorption of CO on the metal surface. As CO concentration decreased to a low value, CO_2 could initially be adsorbed on the spare metal surface and hydrogenated [18–20].

Figure 7 shows XRD patterns of the catalysts $20\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-T_r$ ($T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$) used in the CO-SMET reactions. Metallic Ni phase is observed most evidently

for the sample reduced at 800°C . Table 2 gives phase composition of the catalysts estimated by the Rietveld method. It is clear that error of the phase composition is small ($\pm 0.20\%\sim\pm 0.32\%$), and the fitted Ni/Mg atomic ratio based on the phase composition is quite similar to the feed value, proving the fitting on the two phases of metallic Ni and solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ is reasonable. As shown in Table 2, metallic Ni content is increased with reduction temperature increasing. Correspondingly, the degree of reduction (DR), defined as the fraction of the Ni^{2+} ions reduced into metallic Ni in the total Ni^{2+} ions in the sample, varied from 5.1% to 44.0% as reduction temperature increased from 500°C to 800°C . Thickness of Ni crystallites on the plane (200) ($2\theta = 52.1^\circ$), denoted as $D(200)$, is estimated to be ca. 13.3 nm for the two catalysts with higher Ni contents by use of the Scherrer equation. No exact values could be obtained for the other two catalysts due to their low Ni contents.

The varying of lattice parameter (a) of the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ (cubic crystal system) with reduction temperature is worth noting in Table 2. Different preparation method and starting materials can cause a little difference in value of lattice parameter [1, 21]. Nevertheless, the values of lattice parameter (a) obtained in the present work (see Tables 2–4) are well coincident with the values $4.2123 \text{\AA}\sim 4.1773 \text{\AA}$ reported for the samples of solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ ($1 \geq x \geq 0$) calcined at 1200°C [1]. Since the catalysts $20\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-T_r$ are prepared from reduction of the definite sample $20\%\text{NiO}-\text{MgO}-400$ at the different temperatures $T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$, an increase of metallic Ni content with reduction temperature rising must lead to a simultaneous decrease of x value in the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$. A decreased x value should result in an increased a value according to crystal radii of Ni^{2+} (0.083 nm) and Mg^{2+} (0.086 nm). However, Table 2 shows that a smaller x value corresponds to a smaller a value. One reason may be the difference in reduction temperature. It is reported that heating at a higher temperature led to a smaller value of lattice parameter for MgO [22]. Here the reduction temperatures ($500^\circ\text{C}\sim 800^\circ\text{C}$) were higher than the calcination temperature (400°C). So, the reduction treatment at the different temperatures would have an effect on the value of the lattice parameter. As shown in Figure 3, the NiO entity present in a minor quantity in the sample $20\%\text{NiO}-\text{MgO}-400$ could be reduced first in the reduction process. And then reduction of a part of Ni^{2+} ions in the solid solution was followed [2, 3, 6, 7]. It is clear in Table 2 that sintering of crystallites of the solid solution phase occurred more seriously at higher reduction

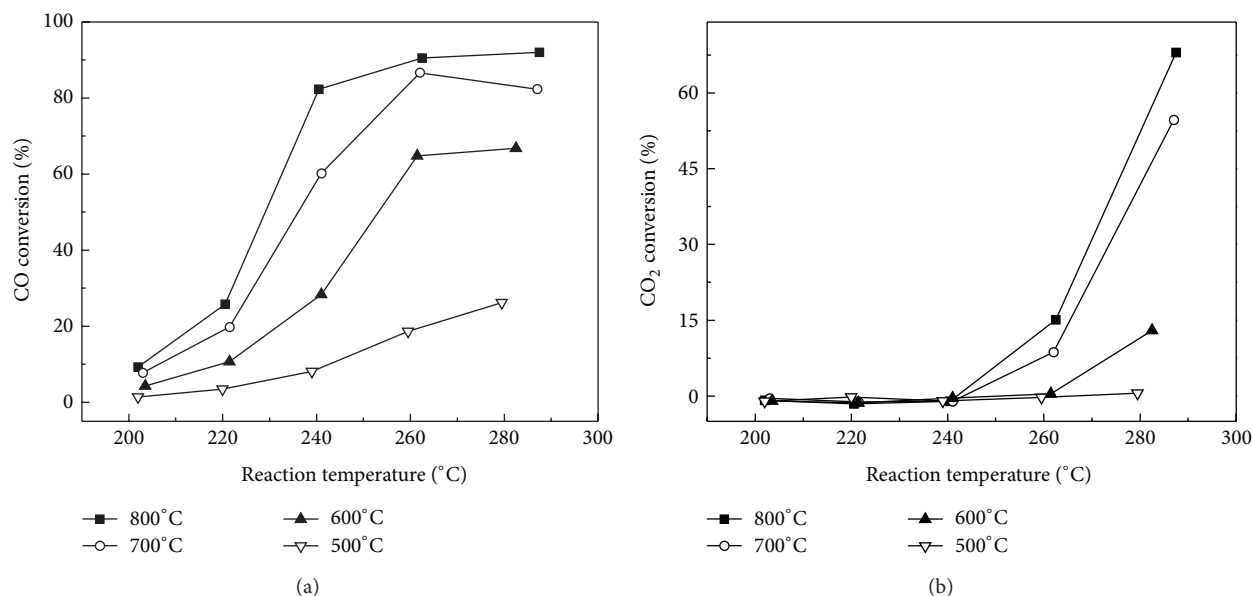


FIGURE 6: Effect of reduction temperature ($T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$) on catalytic activity of the catalysts $20\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-T_r$.

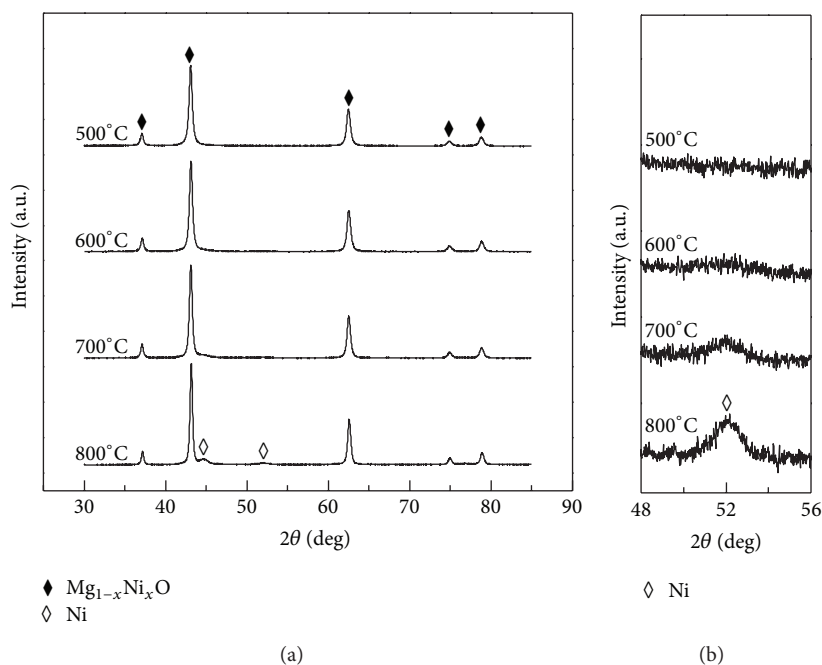


FIGURE 7: XRD patterns of the catalysts $20\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-T_r$ ($T_r = 500^\circ\text{C}\sim 800^\circ\text{C}$) (a) and the locally enlarged XRD peaks of metallic Ni crystallites (b).

temperatures. Crystal domain size (R) of the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ is 23.5 nm when reduction treatment was conducted at 500°C , whereas it is increased to 42.6 nm when reduction treatment was done at 800°C .

In comparison of Table 2 with Figure 6, it is seen that amount of metallic Ni is a crucial factor for CO-SMET reaction. Catalytic activity is enhanced with increasing of amount of metallic Ni in the catalysts. Similar phenomenon was also observed for CO₂ reforming of methane [3].

3.3. Effect of Feed Ni/Mg Ratio. In order to investigate effect of feed Ni/Mg ratio, samples $m\text{NiO}-\text{MgO}-400$ ($m = 10\%\sim 40\%$) were reduced with 85% H_2/N_2 mixture gas at 800°C to prepare catalysts $m\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-800$ ($m = 10\%\sim 40\%$). As seen in Figure 8, a basic trend is that both CO conversion and CO₂ conversion increase with feed Ni/Mg ratio increasing, although the two catalysts with $m = 20\%$ and 30% have a similar catalytic activity. Figure 9 shows XRD patterns of the catalysts $m\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-800$ ($m = 10\%\sim 40\%$) used in

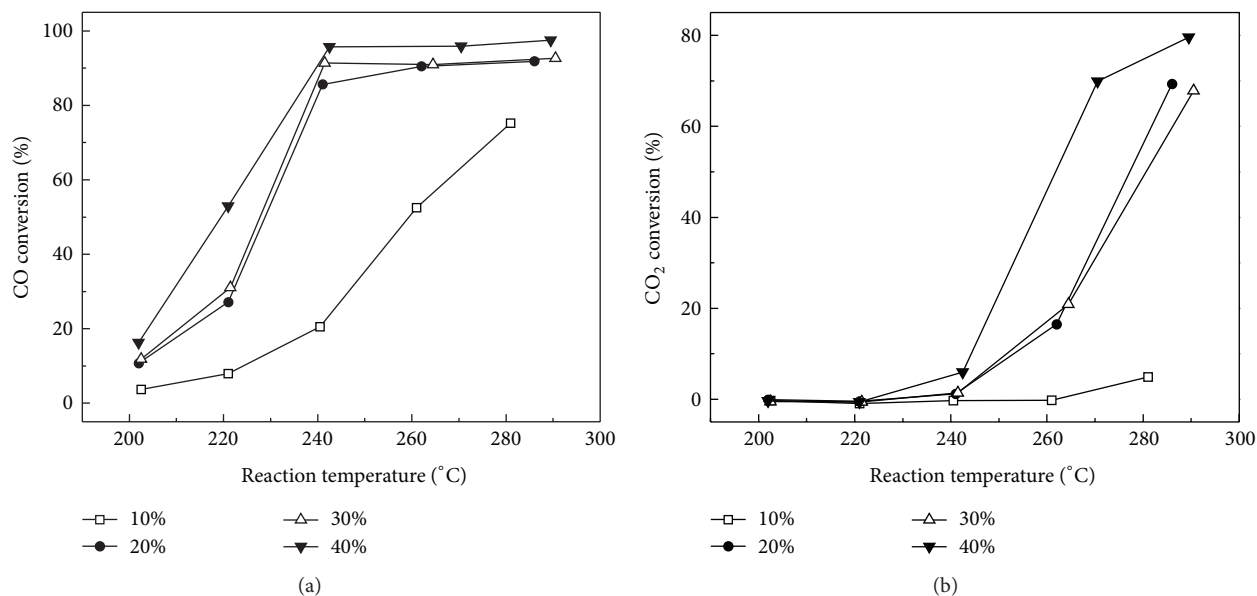


FIGURE 8: Effect of feed Ni/Mg ratio ($m = 10\% \sim 40\%$) on catalytic activity of the catalysts $m\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-800$.

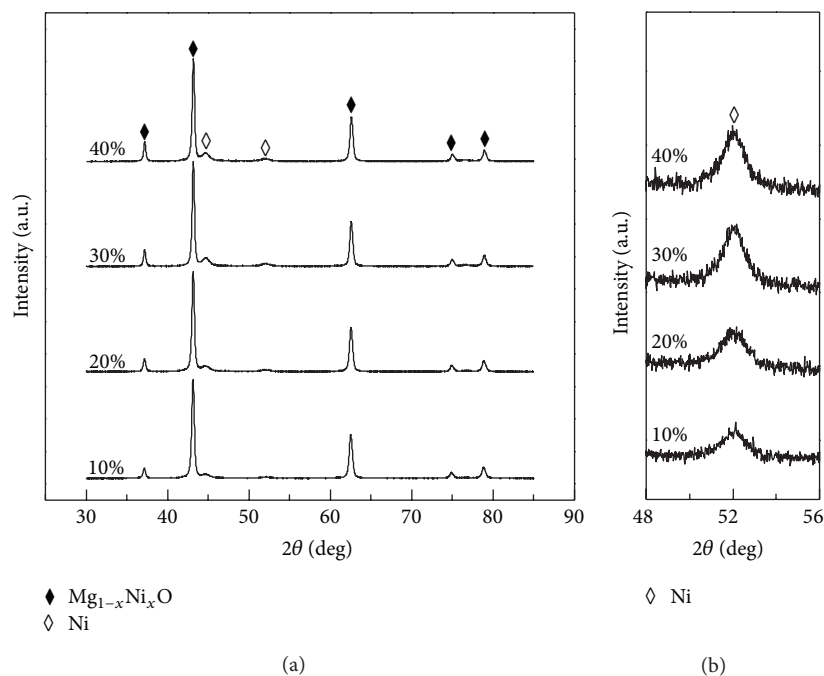


FIGURE 9: XRD patterns of the catalysts $m\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-800$ ($m = 10\% \sim 40\%$) (a) and the locally enlarged XRD peaks of metallic Ni crystallites (b).

the CO-SMET reactions. Table 3 lists phase compositions of the catalysts estimated by the Rietveld method. It is clear that Ni content increased with feed Ni/Mg ratio increasing. Thickness of Ni crystallites on the plane (200) and crystal domain size of the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ were not changed remarkably. It is argued for CO₂ reforming of methane that catalytic activity depends not only on amount

of metallic Ni, but also on its dispersion [21]. This is because the Ni crystallites extracted from the initial solid solution may remain partially embedded in the remaining solid solution [9]. Measurement of dispersion of the Ni crystallites, especially for the catalysts with $m = 20\%$ and 30% , will be conducted in a future work. In addition, lattice parameter (a) of the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ decreases

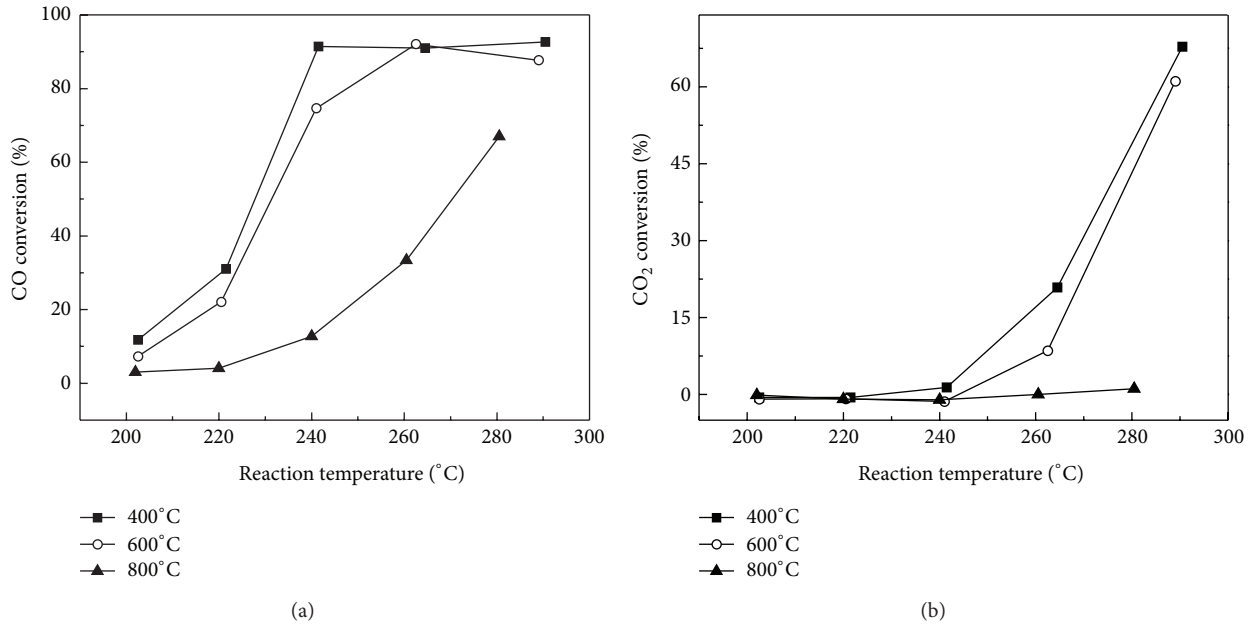


FIGURE 10: Effect of calcination temperature ($T_c = 400^\circ\text{C}\sim 800^\circ\text{C}$) on catalytic activity of the catalysts $30\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-T_c-800$.

TABLE 3: Effect of feed Ni/Mg ratio ($m = 10\%\sim 40\%$) on phase composition of the catalysts $m\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-400-800$.

m (%)	$\text{Mg}_{1-x}\text{Ni}_x\text{O}$			Phase composition (wt%)			DR (%)	Ni $D(200)$ (nm)	Ni/Mg atomic ratio	
	x	a (Å)	R (nm)	$\text{Mg}_{1-x}\text{Ni}_x\text{O}$	Ni	Error			Fitted	Feed
10	0.0098	4.2124	44.0	95.99	4.01	0.14	74.7	12.2	0.039	0.070
20	0.0602	4.2105	43.9	93.54	6.46	0.19	45.3	13.9	0.117	0.137
30	0.1094	4.2086	47.7	90.53	9.47	0.17	41.8	11.3	0.211	0.203
40	0.1548	4.2066	45.1	90.05	9.95	0.19	35.7	13.3	0.285	0.262

with increasing of the x value, consistent with the fact that radius of Ni^{2+} ion (0.083 nm) is smaller than that of Mg^{2+} ion (0.086 nm).

3.4. Effect of Calcination Temperature. Samples $30\%\text{NiO}-\text{MgO}-T_c$ ($T_c = 400^\circ\text{C}\sim 800^\circ\text{C}$) were reduced with $85\%\text{H}_2/\text{N}_2$ mixture gas at 800°C to obtain catalysts $30\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-T_c-800$ for CO-SMET. Figure 10 clearly shows that low calcination temperature is beneficial for conversion of CO and CO₂. Figure 11 shows XRD patterns of the catalysts $30\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-T_c-800$ ($T_c = 400^\circ\text{C}\sim 800^\circ\text{C}$) used in the CO-SMET reactions. Phase compositions of the used catalysts estimated by the Rietveld method are listed in Table 4. It is clear that Ni content is greater in the catalyst experienced with a preceding calcination at a lower temperature, which is in agreement with the report [12]. Thickness on the plane (200) of the Ni crystallites, formed on reduction of the samples $30\%\text{NiO}-\text{MgO}-400$ and $30\%\text{NiO}-\text{MgO}-600$, is constant at ca. 11.4 nm. Meanwhile the crystal domain sizes of the two remaining solid solutions $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ are also similar at ca. 47.5 nm. In comparison, the sample $30\%\text{NiO}-\text{MgO}-800$ is the most difficult to be reduced, forming the least amount of Ni crystallites on the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$. This remaining solid solution has a larger x value and a smaller

lattice parameter (a) and also a larger crystal domain size of 54.5 nm. Again, it is seen that the fitted Ni/Mg atomic ratio based on the phase composition is quite similar to the feed value, proving the fitting on the two phases of metallic Ni and solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$ by the Rietveld method is reasonable.

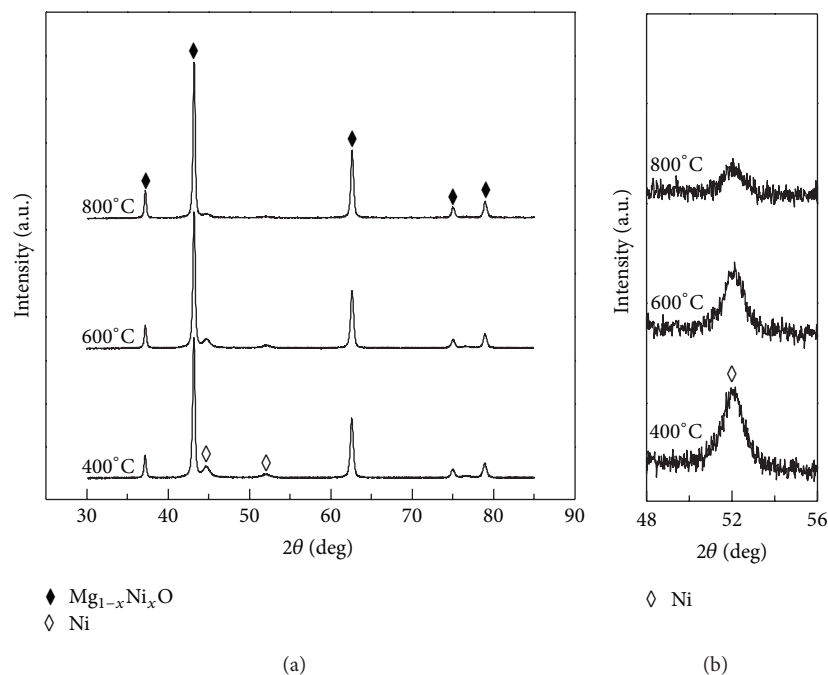
4. Conclusions

The samples NiO-MgO calcined at 400°C were composed of solid solution $\text{Mg}_{1-y}\text{Ni}_y\text{O}$ as the main phase and a minor amount of NiO. Amount of the NiO decreased as calcination temperature increased. TPR analysis is useful to detect NiO entity in minor amount in the case XRD peaks of NiO are overlapping with those of MgO and solid solution $\text{Mg}_{1-y}\text{Ni}_y\text{O}$ phases. XRD peak overlapping makes it difficult to estimate phase composition exactly for samples NiO-MgO by the Rietveld method.

Phase composition of the catalysts $\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}$ prepared by reducing the samples NiO-MgO in H_2/N_2 mixture gas at $500^\circ\text{C}\sim 800^\circ\text{C}$ was estimated by the Rietveld method. Amount of metallic Ni formed in the catalysts is dependent on reduction temperature, feed Ni/Mg ratio, and calcination

TABLE 4: Effect of calcination temperature ($T_c = 400^\circ\text{C}\sim 800^\circ\text{C}$) on phase composition of the catalysts $30\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-T_c-800$.

T_c ($^\circ\text{C}$)	$\text{Mg}_{1-x}\text{Ni}_x\text{O}$			Phase composition (wt%)			DR (%)	Ni $D(200)$ (nm)	Ni/Mg atomic ratio	
	x	a (\AA)	R (nm)	$\text{Mg}_{1-x}\text{Ni}_x\text{O}$	Ni	Error			Fitted	Feed
400	0.1094	4.2086	47.7	90.53	9.47	0.17	41.8	11.3	0.211	0.203
600	0.1166	4.2087	47.4	92.76	7.24	0.20	33.6	11.5	0.199	0.203
800	0.1393	4.2070	54.5	97.03	2.97	0.20	14.4	—	0.189	0.203

FIGURE 11: XRD patterns of the catalysts $30\%\text{Ni}/\text{Mg}_{1-x}\text{Ni}_x\text{O}-T_c-800$ ($T_c = 400^\circ\text{C}\sim 800^\circ\text{C}$) (a) and the locally enlarged XRD peaks of metallic Ni crystallites (b).

temperature. Thickness of Ni crystallites on the plane (200) appeared to have a constant value of 12.5 ± 1.3 nm in the catalysts where the XRD peak on the plane (200) was strong enough to allow an exact calculation by the Scherrer equation.

CO conversion was generally enhanced by an increased amount of metallic Ni. And CO_2 hydrogenation occurred initially at reaction temperature of 240°C over the catalysts. Dispersion of Ni crystallites on the support (i.e., the remaining solid solution $\text{Mg}_{1-x}\text{Ni}_x\text{O}$) is expected to have an effect on catalytic activity and will be studied in the future.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

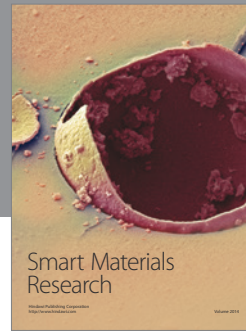
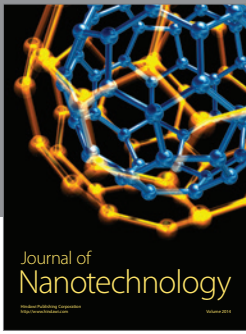
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